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THE SPECTRA OF GASES AND METALS AT HIGH TEMPERATURES.

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IN previous papers I have described certain phenomena which arise in the employment of photography in spectrum analysis — especially the phenomenon of the appearance of dark lines instead of bright lines in the spectra of electrical discharges in Geissler tubes.

The application of photography to spectrum analysis has the great advantage of giving an impersonal record of certain phenomena by substituting a chemical method of investigation for eye observations.

We thus obviate the personal equation of the observer; but unfortunately we bring in vagaries of the photographic plate.

The photographic plate can be called an instrument with an infinite number of adjustments. The molecular movements of the silver molecules under different degrees of electric stimulation can give us a great number of combinations. In short, the photographic plate does not afford a simple method of observing the effects of different waves of light on the molecules of matter. Its complicated nature is well shown by the records it gives of the intensity of light which provokes its action. It has long been recognized that the blackness of a negative is no criterion of relative intensity of light; in other words, that the negative cannot be employed as a photometer except in the crudest way. A method of illustrating this fact is given in this paper.

The photographic method of observation in spectrum analysis, however, is naturally of great use in preserving records of a great multiplicity of phenomena; but we have to be on our guard in interpreting these phenomena; for, unlike the galvanometer or the bolometer, our recording instrument is complex. Furthermore, when we use an electric spark to agitate the molecules of a gas or the molecules of a metal we use one complicated means to study a still more complicated phenomenon. When one asks what is the spectrum of water vapor, one must define the conditions of the electrical stimulus; for one can, by increasing the range of this electrical stimulus, run through a gamut of dissociations and recombinations. One never deals with a strictly pure vapor or gas.

The spectra of metals in atmospheric air are the visible evidence of extremely complicated chemical reactions due to the reaction of the metallic vapor and the gases of the atmosphere. The spectra of gases also in narrow containing vessels of glass or of quartz, are modified by the walls of these vessels when the temperature of the gases is very high; moreover, the ordinary method of obtaining photographic spectra either of metals in air or rarefied gases by long continued discharges produced by the Ruhmkorf coil of transformers masks certain fundamental reactions.

It is therefore desirable to study the effect of known quantities of energy successively applied to produce spectra either of metals or gases. This can best be accomplished by charging a condenser to a known amount by a known electromotive force, and by discharging the condenser between terminals of metals either in air or in gases. If the spectra produced in this manner by discharges varying from one to any desired number are photographed on the same plate and treated alike in the same developer, the ground may be prepared for some generalization of the extremely complicated reactions I have mentioned; I believe that this method is a fundamental one to use if order is to be brought out of the chaos of spark spectra.

I have applied this method in the following manner: A storage battery of from ten thousand to twenty thousand cells is employed to charge a condenser — .1 to .3 microfarad. By a simple mechanical appliance the condenser is detached from the poles of the battery, and is discharged between suitable terminals. Although it is impossible to avoid a slight spark at the moment of making contact with the receiving system, an approximately equal quantity of electricity is communicated to this system at each discharge. The method also permits of a definite control.

In order to photograph on the same plate the spectra produced by successive discharges the photographic plate must be slid vertically from one position to another, at the focus of a Rowland grating. The most convenient arrangement for the study of gaseous spectra is to employ a grating of short focus, and to enclose it in a light, tight box. For compactness, and to dispense with a dark room, I have employed the method of mounting the grating in such a manner that the normal to the ruled surface passes through the slit. The camera swings on the arc of a circle described by an arm of half the radius of the grating. This arm is pivoted at a point half way between the ruled surface and the slit. In Figure 1, G is the grating, M the point midway between the grating and the slit, C the camera swinging on the arc described from M. Figure 2 gives a side view and elevation of the camera. P is the photographic plate, O an opening closed by a slide operated by a lever arm which engages with A. The plate holder closed by another slide S, can move up or down in parallel ways. In Figure 1 is shown a lever arm LM with fulcrum at F. This lever lifts another lever AM, which in turn lifts or closes the shutter A, Figure 2. The lever LM is outside the dark box, and the operation of exposing the plate and closing the camera can be performed without opening the box. The method which Rowland used in mounting the grating is undoubtedly preferable to the above, when an accuracy greater than one-tenth of an Ångstrom unit is aimed at. The advantage, however, of the method I have employed is in its compactness and in the possibility of working in a light room; moreover, in gas spectra an accuracy even to one Ångstrom unit is often respectable.

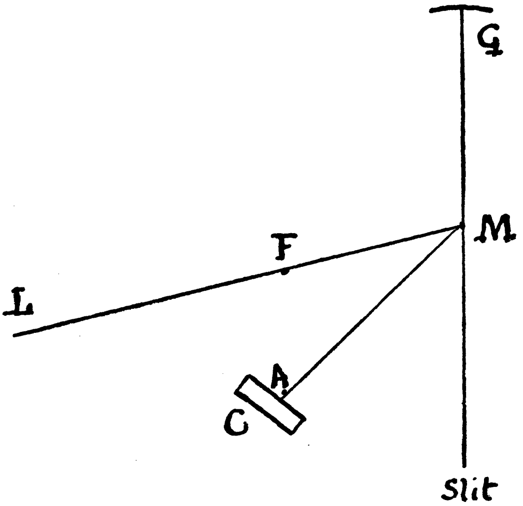


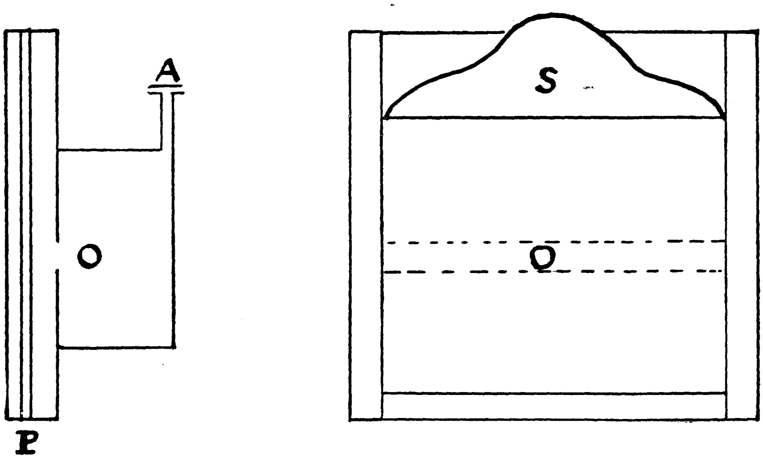
Fig I

The capillaries which I used in this investigation may be termed scientific electric furnaces for studying by photography the spectra of gases at high temperatures, and the spectra of the vapor of metals at such temperatures in rarefied media. These capillaries were from four to five inches long, with internal bore of from one millimeter to one and a half millimeters. The metallic terminals were approximately of the same diameter as the capillary, and were inserted in the capillaries until the distance between the ends of the terminals in the capillaries varied from one centimeter to two millimeters.

The capillaries were made of lead glass; of German glass which did not contain an appreciable amount of lead; and of quartz.

When an electric discharge occurs near a luted joint or surface a species of what may perhaps be termed electric distilling takes place. If silicate of soda is the luting agent, the vessel containing the rarefied gas becomes coated with a white film which shows the soda reaction; if a preparation of gums or shellac is used an organic film is obtained.

Fig 2



By the use of long capillaries in which the discharging metallic points are several inches from the points of luting this distilling action can be entirely avoided. It is therefore not necessary to use platinum for closing the ends of the capillaries in order to exhaust the latter. Quartz capillaries can be used without fear of introducing impurities from the luting agents, if long terminals are employed with the luting points at a distance from the discharge points.

In the use of capillaries with metallic terminals almost in contact with the walls of the containing vessels there must necessarily be spectra, one would suppose, arising from the substances of these walls and a combination of these substances with the rarefied gases. It is also possible that even if the walls do not show a characteristic spectrum they may influence by a species of katalytic action the reaction between the rarefied gases and the vapors of the metallic terminals.

It is interesting to observe the appearance of successive orders of spectra photographed by the camera I have described with progressively increasing strengths of electrical discharges as well as repeated discharges of the same strength. When, for instance, the capillaries are filled with rarefied water vapor one generally obtains with comparatively weak electrical discharges hydrocarbon spectra which possibly arise from traces of carbonic acid in the capillaries or from traces of grease in the stopcocks of the pump. These banded spectra decrease in strength as the strength of the electrical discharges increases, and finally disappear with powerful discharges. The hydrocarbon combinations are evidently broken up and new reactions and combinations enter. We therefore may not be able to recognize in these new reactions the presence of a simple component.

In the study of the spectra of heavenly bodies which may be considered from the point of view of furnaces, this fact I think should be borne closely in mind. Substances may be present which do not appear in the spectra observed at great distances; for the relative brightness of metallic lines and gaseous lines is much modified by the combinations which enter in an environment of high temperature.

Figure 3 (the photographs are reproductions of the negatives, and are not positives) is a reproduction of the spark spectrum of calcium in the neighborhood of the H.H. lines of the solar spectrum taken by the method of successive discharges of known amounts of electrical energy. The discharges ran from one to five. It is interesting to notice on the negatives that the photometric intensity of the lines estimated by the blackness is not directly proportional to the amount of energy. Thus the spectrum produced by four discharges is not twice as intense as that produced by two discharges. It is noticeable, also, that the calcium lines, wave lengths 3737 and 3706, are stronger on the negative than those which coincide with the H.H. lines, and always appear with these lines.

Figure 4 is a negative of discharges running from one to four in a Geissler tube of glass which did not contain an appreciable amount of lead in its composition. The capillary was two millimeters, internal diameter, and four inches in length. The pressure of hydrogen was one millimeter. It is noticeable that the lines which coincide with the H.H. lines are not accompanied by the lines, wave lengths 3737 and 3706;

although the intensity of the lines coinciding with the H.H. lines, if they were calcium lines, would require the presence of these lines.

A series of experiments was undertaken with metallic terminals one centimeter apart, in lead glass. The diameter of the capillary varied from one to two millimeters. A spectrum similar to that of Figure 4 was obtained with the addition of certain lead lines, several of which were reversed on the side toward the ultra violet. The portion of these lines not reversed broadened toward the red end of the spectrum; and this broadening increased with the intensity of the discharge (Figure 7). No calcium lines appeared. When cadmium terminals were used many of the cadmium lines were reversed, and here also the bright portion of these lines was much broadened. In the case of cadmium no other lines was observed (Figure 6). The gaseous ions contributed little or nothing to the photographic effect.

When iron terminals were employed no iron lines were obtained even when the terminals were only three millimeters apart; nevertheless the lines and bands usually attributed to silicon came out with great intensity. When, however, aluminum terminals were substituted for iron terminals, aluminum lines, together with the supposititious silicon lines, were obtained. It was noticeable that the two lines coinciding with H.H. lines of the solar spectrum did not appear, while the two characteristic aluminum lines between the H.H lines came out reversed. The lines corresponding with the H.H. lines always appeared when a discharge of like intensity produced the spectrum of aluminum in air.

The iron of which the terminals were made was ordinary soft iron, with a melting point not far from 1100°, while the melting point of aluminum is between 700° and 800°. If the silicon is volatilized it is difficult to see why the iron gave no spectrum, while the aluminum yielded one, for there is not a very great difference between their melting points.

Another series of experiments then were made with metallic terminals in quartz capillaries varying in internal diameter from two to three millimeters, the terminals being one centimeter apart. The same spectra were observed as are represented in Figure 3, with an absence of the lines corresponding with the solar H.H. lines. This absence was noticeable, also, when metallic terminals were one centimeter apart in lead glass. Iron terminals gave no iron lines in the quartz tubes, while aluminum lines appeared when aluminum terminals were used instead of iron terminals.

When the metallic terminals were placed three millimeters apart in the quartz tubes the light from the tubes was very feeble, traces of metallic spectra appeared, and the walls of the quartz capillaries were speedily covered with thin films of the metals; even at the first discharge, before there was a sensible obscuration due to the formation of the films, there was no evidence of gaseous spectra. The main discharge appeared to be carried over by the metallic vapor and no dissociation of the gas was evident.

Measured by definite amounts of electrical energy, the rating of the intensity of spectral lines differs totally from existing eye estimates. The lines which coincide with the H.H. lines in the spectra of the metals with high melting points generally came out first on the photographic plate when the method of successive discharges was employed.

Rarefied nitrogen gave far less light than hydrogen, water vapor, or oxygen. When oxygen was employed, characteristic groups of doublets were obtained like the A and B groups in the solar spectrum. The heads of these groups apparently coincided with the middle of broad lines shown in Figure 4. The middle of these broad bands or broad lines coincides also with narrow lines usually attributed to silicon. Are certain lines attributed to silicon really oxygen lines? Salet, and also Rowland, assign the photometric intensity of 4 to the lines 4131.5 and 4126.5, 3 to the lines 3905 to 3855.7, and 10 to the line 2881. When the lines given on plate 4 and those on plate 7 are photographed on the same plate by the same number of discharges and are compared in regard to intensity, the rating is completely reversed, the lines at 4131.5 and 4126.5 and 3905 to 3855.7 being 10, and the line 2881 being three or four.

The broadening of what have been considered metallic lines in rarefied cases I consider a most interesting phenomenon. Only the strong lines of the spark spectrum of the metal in air seem to be reversed under the effect of powerful discharges in rarefied gases. This broadening appears to be the evidence of reactions between the vapor of the metal and the surrounding gases. In this connection it is well to bear in mind the fact that metals continue to give off gases for a long time when submitted to powerful electrical discharges in vacuum tubes. This has been shown by Dr. Rollins of Boston in his researches on X-rays.

These nascent gases are in condition to exhibit complicated reactions with the strongly heated metallic terminals.

My experiments lead me to strongly doubt conclusions drawn from the apparent absence of this or that element in the spectra of stars; for there is a strong possibility that reactions enter which may mask the presence of this gas or that metal.

The conclusions of my work thus far are as follows:

1. The metallic lines due to terminals in rarefied hydrogen, and rarefied air, when these terminals are one centimeter apart in glass or quartz capillaries, exhibit a reversed action. When this takes place it is generally coincident with the position of the line when the spectrum is taken in air, while the spectrum of the line on the least refrangible side is much broadened. This seems to indicate a gaseous product; an oxidization or hydration due to the dissociation of the air and water vapor present.

2. Highly heated rarefied hydrogen and rarefied air passing over containing walls of glass or amorphous silica give broad bands which apparently coincide with narrow silicon lines of far lesser intensity. These also I attribute to the dissociation of air and water vapor. The brilliancy of the light produced in this reaction is far greater when there is an excess of hydrogen in the tubes than when rarefied air fills them. It is a question whether lines produced by metals like silicon in their difficulty of volatilization in air are really due to the metals. I am inclined to attribute some of them to the environment; that is, to a reaction between the metal and the gases present.

3. Spark spectra of metals appear to represent complicated reactions of gases with the metallic vapor.

4. Metallic vapor carries the main portion of an electric discharge when these terminals are within three millimeters of each other in rarefied hydrogen or rarefied air. The gaseous ions, if the dissociation occurs, give little light.

5. The broadening of the light accompanying the reversed lines, if unsuspected, might lead one to conclude that a shift of the bright portion had occurred.

6. Since the iron lines do not appear under what seems favorable conditions while aluminum lines appear; while in other cases gaseous lines mask metallic spectra, it seems desirable to be cautious in regard to speculations in regard to types of stars.

7. Whatever may be the cause of the reversals of lines observed in narrow capillaries of glass or of quartz, it seems to me that it is a fact which should be reckoned with in photographic study of stars, especially in the case of sudden changes of light.

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Figure 7.

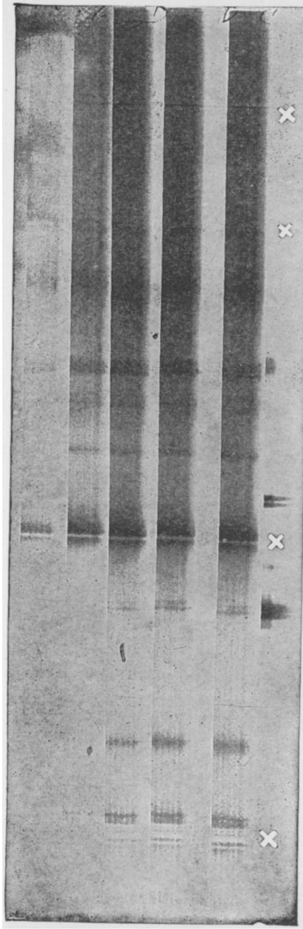

Figure 6.

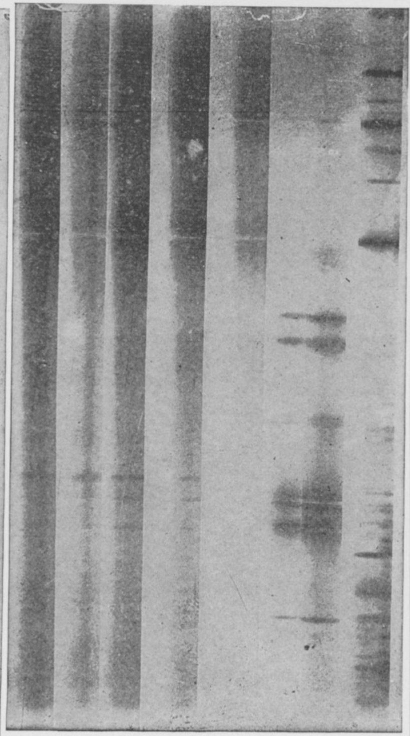

Figure 5.

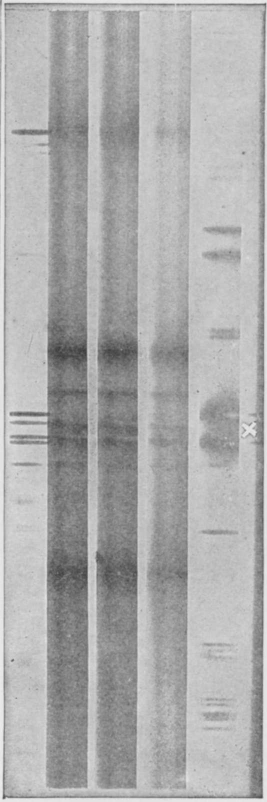

Figure 4.

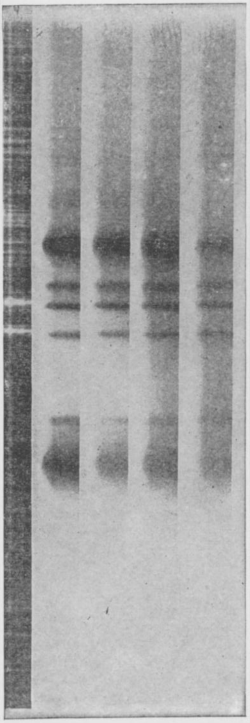

Figure 3.